FERTILIZERS TECHNOLOGY

CHEM 0905554

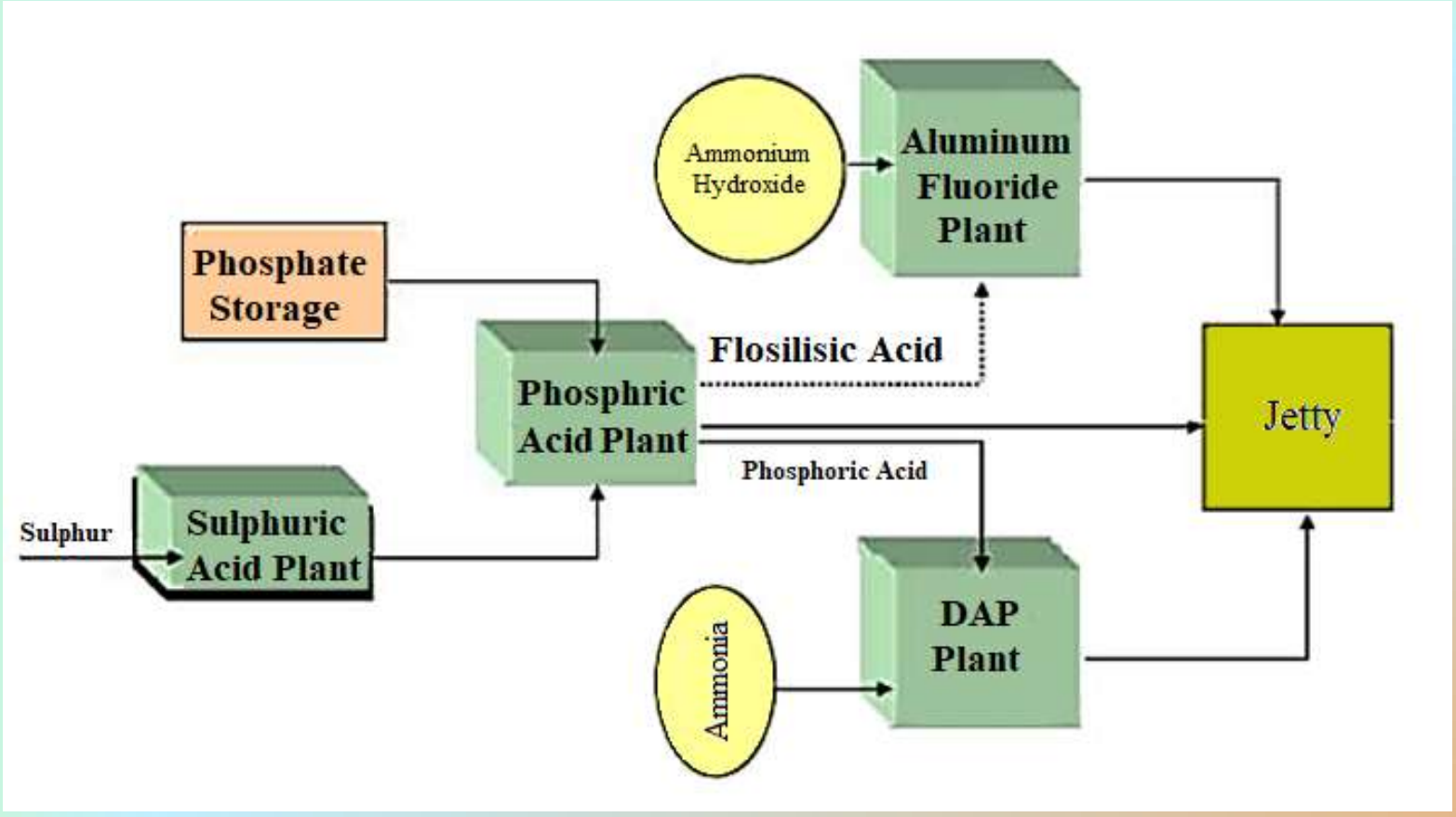
First Semester 21/22

CHAPTER 7

DIAMMONIUM PHOSPHATE PRODUCTION


FINE PINK
GRANULATED WHITE
#5 PINK GRANULATED
CRYSTALIZED WHITE
PINK PRODUCT

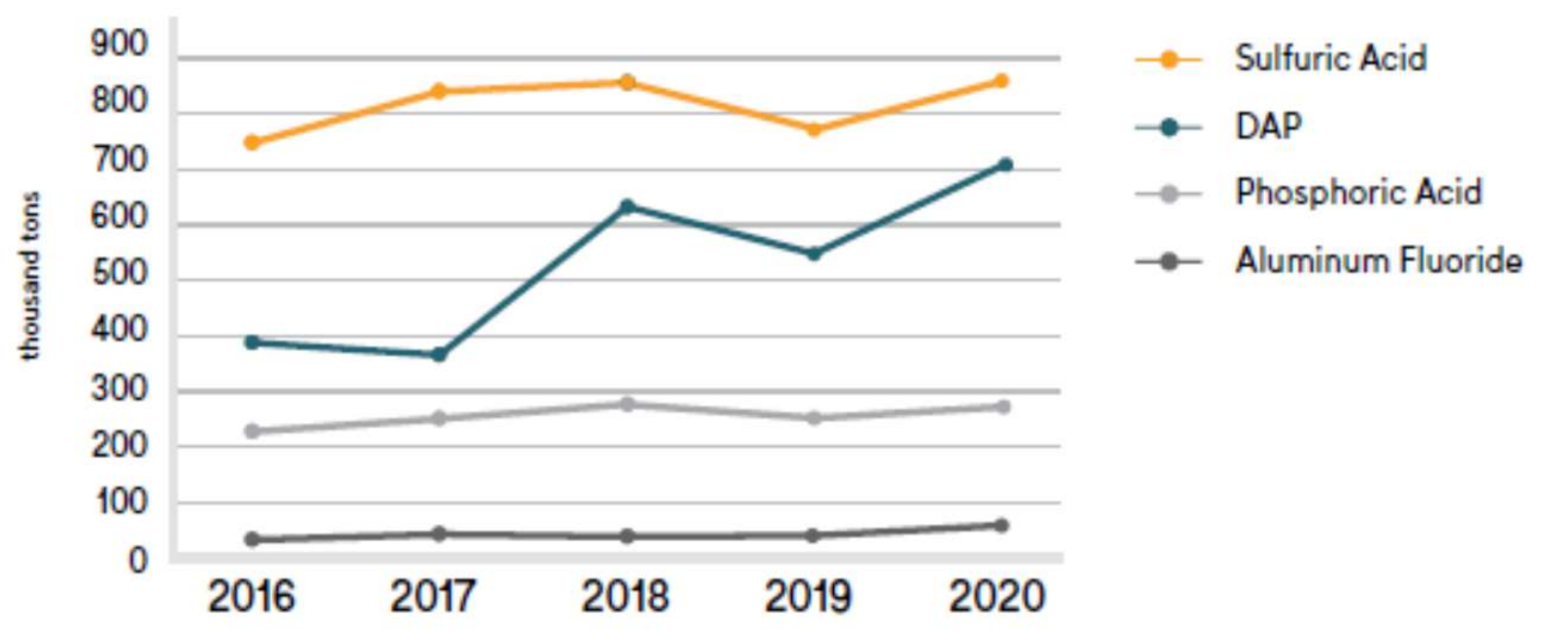
JORDAN PHOSPHATE MINES INDUSTRIAL COMPLEX



QUANTITIES PRODUCED at the INDUSTRIAL COMPLEX IN AQABA

Product	2020	2019	2018	2017	2016
DAP	707	550	632	379	396
Phosphoric Acid	282	252	281	264	228
Sulfuric Acid	863	780	856	839	738
Aluminum Fluoride	10	6	6	6	4

QUANTITIES PRODUCED at the INDUSTRIAL COMPLEX IN AQABA



INTRODUCTION

- Di-Ammonium Phosphate (DAP), as a fertilizer is produced by Jordan Phosphate Mines Company at a capacity reaching to 3000 metric tons daily.
- It contains 18% Nitrogen, and 46% Phosphorus pentoxide, which is soluble granular, and leads to easy absorption by the plants and vegetation.
- It can be used by farms machinery, for all crops and trees, and for either rain-fed or irrigated lands.
- The material of composition are ammonia, wet-process phosphoric acid, sulfuric acid.
- Raw Materials:

    1. Wet process phosphoric Acid.
    2. Ammonia.

PROPERTIES OF DAP

- Molecular formula: $(NH_4)2HPO_4$
- Appearance: Brown to black granules
- Molecular weight: 132.07
- Specific gravity (H_2O = 1): 1.619 (heavier than water)
- Melting point: Decomposes at 155°C (311°F)
- Solubility in water: 588 g/L at 20°C (68°F)
- Odor: Odorless or slight ammonia odor
- Physical state: Solid
- pH: Approximately 8 (1% aqueous solution)

THE PROCESS

- The process is initiated by charging the reactor with phosphoric acid and gaseous ammonia.
- In the reactor the phosphoric acid is partially neutralized by the ammonia.
- Anti foam is added to the reactor to control the potential foaming hazard, such as olives oil.
- The reaction generates heat which is utilized to evaporate water from the slurry.
- Control is maintained over the heat of reaction by adding process water from the tail gas scrubber.
- This water dilutes the slurry and maintains it in a readily flowable state.

THE PROCESS

- The slurry moisture content must be high enough for pumping (16-20) and low enough for high production rates.
- From the reactor, the slurry is pumped to the granulator where it is distributed over a rolling bed of recycle material.
- The recycle consists of cyclone dust, undersize granules, crushed oversize and some product size granules.
- Simultaneously, liquid ammonia is sparged in the granulator to complete the acid neutralization.
- The ammoniated granules are then discharged to the dryer.

THE PROCESS

- The granulator vent air is drawn into a duct where it combines with vent out from the reactor.
- The flow enters the reactor–granulator scrubber, where any un-reacted ammonia is reclaimed.
- The scrubber also serves to control fluorine emission to atmosphere.
- In the dryer, hot air flowing co-current with the granules reduced the granule moisture to approximately 1%.

THE PROCESS

- The stream out of the dryer are elevated to the screen feed conveyer the material then flows to the screens where oversize (+6 mesh) and undersize granules (-16 mesh) are separated.
- The oversize particles flow to chain mills where they are partly crushed and discharged directly to the recycle conveyer.
- Product size-granules flow to the product surge bin.
- The product flows from the surge bin by means of a variable speed conveyor and deliver it in the cooler.
- The cooler lowers the temperature of the product.

THE PROCESS

- From the cooler, the product flows to an elevator and then to a polishing screen where oversize granules or fine are removed and directly back to the recycle conveyor and the finishing product is sent to the storage area.
- The exhaust stream of saturated air vented to the atmosphere after cleaning of objectionably impurities by means of a primary scrubbing system and the tail gas scrubber.
- The primary scrubbers act as dust absorbers and also reclaim any un-reacted (NH_3).

THE PROCESS

- In the case of DAP, the scrubbing liquid contains phosphoric acid but when MAP is in process the scrubber liquid is water.
- The tail gas scrubber receives the exhaust from the primary system and acts as an independent gas cleaning system, it uses re-circulated water as its scrubbing medium.
- The exhaust from the tail gas scrubber is vented to the atmosphere.

PROPERTIES OF DAP

- The main chemical compounds present in the granular products are:

Ammonia	NH3
DAP	(NH4)2HPO4
MAP	(NH4)2H2PO4
A.S.	(NH4)2SO4
Sulfuric Acid	H2SO4
Phosphoric Acid	H3PO4
Flousilicic Acid	H2SiF6
Gypsum	CaSO4.2H2O
Iron Phosphate	FePO4
Ammonium Fluoride	NH4F
Sodium Hydroxide	NaOH
Aluminum Phosphate	AlPO4

REACTION

$$NH_3 + H_3PO_4 \longrightarrow NH_4H_2PO_4 + \text{heat}$$

- After MAP is formed and if ammonia is in excess

$$NH_3 + NH_4H_2PO_4 \longrightarrow (NH_4)_2HPO_4 + \text{heat}$$

- Excess ammonia in the outgoing gases is recovered by reaction with phosphoric acid in the primary scrubbers.
- The reactor is operated to form specific mixture of MAP and DAP, this is because the mixture of the two is much more soluble than either one alone and easier to pump at lower moisture contents.

REACTION

- The ammonia to phosphoric acid mole ratio in the reactor is 0.6 (MAP) or 1.4 (DAP).
- Specific gravity of slurry 1.53 and temperature range (110°C) DAP to (115°C) MAP.

$$NH_3 + H_2SO_4 \longrightarrow (NH_4)SO_4 + \text{Heat.}$$

- All of the fertilizer products to some extent have ammonium sulfate since phosphoric acid normally contains (3-4%) sulfuric acid.
- The physical action that takes place in the granular is the coating and sticking together of dry recycle particles with the liquid slurry.
- These coated and agglomerated particles are then rounded by the rolling action of the acid.

REACTION

- Granulated product leaves the granulator at about 85 to 100°C and it is fed to a rotary dryer where the granules are hardened by removal of moisture.
- Anhydrous ammonia comes in two forms liquid and vaporized.
- The liquid form is more dangerous from the safety standpoint, because it has a high coefficient of expansion.
- When it is confined in a pipeline or in a full tank and warms up it will exert enormous pressure that will tend to either open a safety valve or break the line at the weakest point.
- If it is allowed to be released into air, it lowers its temperature at once to -35°C and therefore it will freeze anything containing moisture that it touches.

REACTION

- The phosphoric acid can cause sever burns when it is hot, if the acid is both hot and concentrated then the danger will be more severe due to the dehydrating and effect.
- The sulfuric acid is a colorless to cloudy liquid which must be properly handled.
- Concentrated solutions are rapidly destructive to body tissue with which they come in contact producing severe burns.
- Contact with eyes will case severe damage and it may result in total loss of sight.
- Always we must wear required protective equipment.

MAIN EQUIPMENT

REACTOR

- The reactor functions as a pre-neutralizer, Ammonia vapor, recycled acid, and phosphoric acid are metered to the reactor and phosphoric acid is partially neutralized by the ammonia.

MAIN EQUIPMENT

GRANULATOR

- Three process streams are charged to the granulator they are:

  1- The slurry from the reactor. 2- Recycle granules. 3- Liquid ammonia.

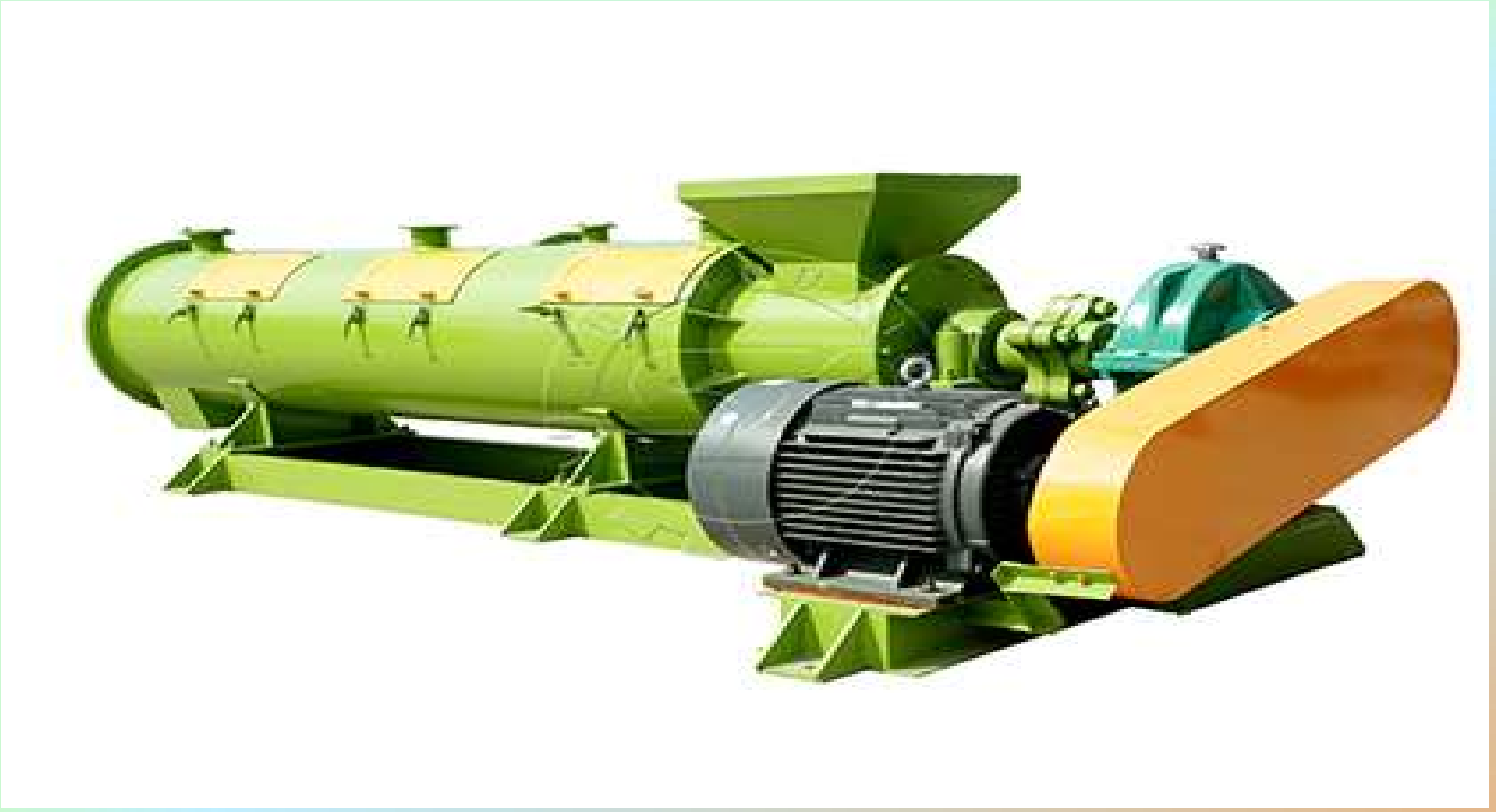
- Two major events occur simultaneously within the granulator:

  1- The ammonia reacts with the slurry to form either DAP or MAP.

  2- The coating of the recycles granules with the reactor slurry coupled with the rotating action of the granulator generates uniform spherical particles.

- Vapors and dust are discharged to the reactor-granulator scrubber.

GRANULATOR

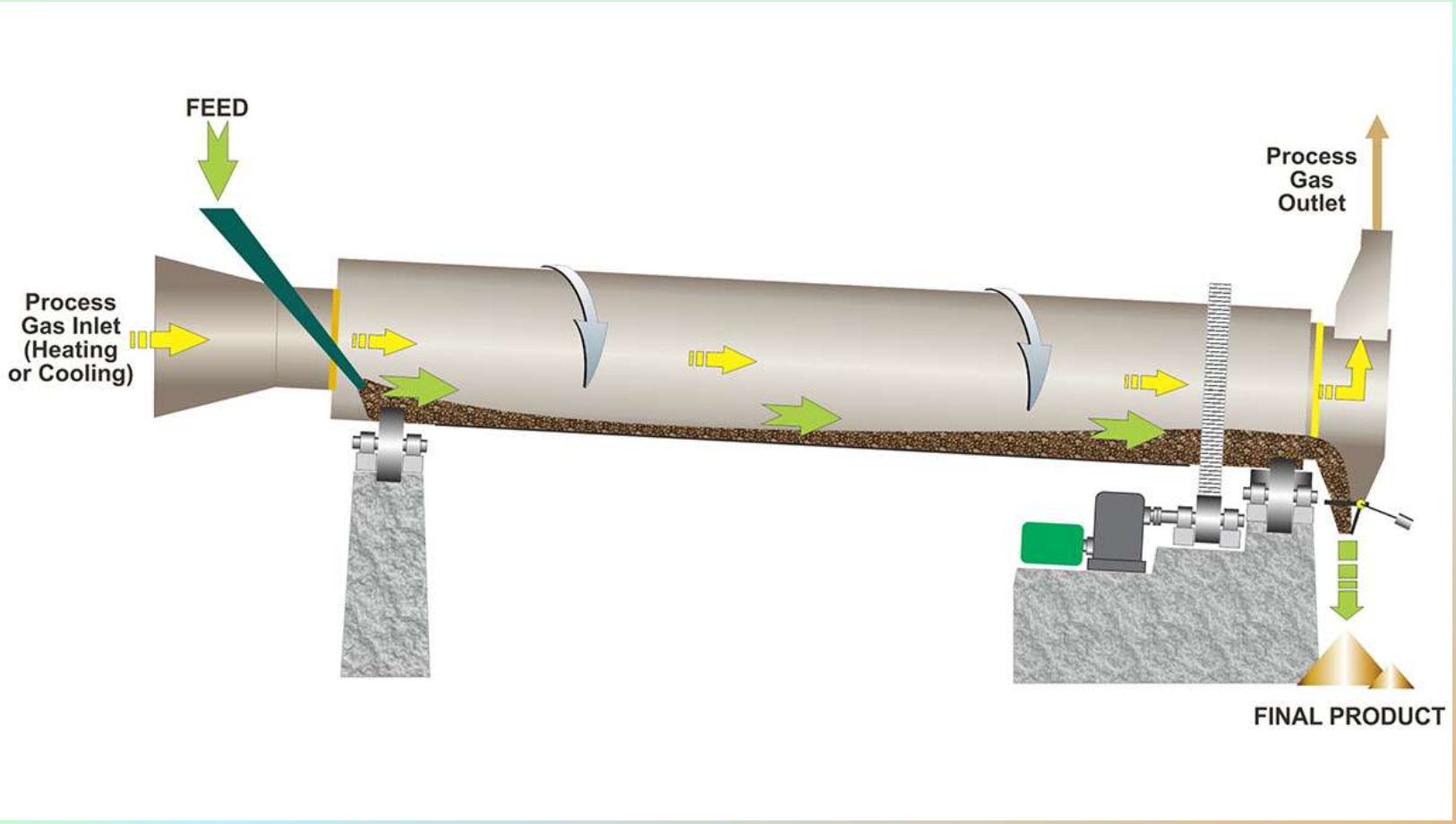


MAIN EQUIPMENT

DRYER

- The discharged from the granulator and combustion gases from the oil-fired combustion chamber, these two streams flow co-currently through the dryer.
- The temperature of air varies from app. 205 to 324^{o}C, the dryer is oriented at an angle to the horizontal and this downward slope with the aid of an inducted draft gives the granules their forward motion.
- The function of the dryer is to remove moisture from the product.

DRYER


FEED
Process
Gas Inlet
(Heating
or Cooling)
Process
Gas
Outlet
FINAL PRODUCT

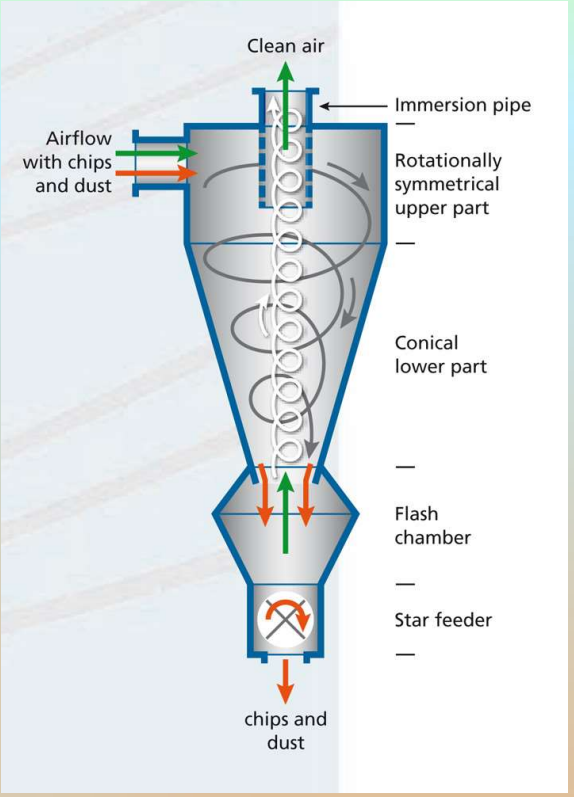
MAIN EQUIPMENT

COOLER

- Two process streams enters the rotary cooler.
- They are the discharge from the dryer and cool air.
- The function of the cooler is to lower the temperature of the product, this reduces ammonia loss and the product agglomeration during storage.
- The product depending on the grade enters the cooler at 85 to 100°C and exit at approximately 54°C, the cool air which flows counter current to product steam enters at about 30°C or less.

CYCLONES

- Dryer cyclone, Dust-vent cyclone, Cooler cyclone.
- The vent air enters the cyclone tangentially and is subjected to a centrifugal spinning action which throws the larger dust particles against the cyclone wall.
- These large particles flow by gravity down the cyclone walls to the double-flap discharge valve from where they are discharged to the recycle conveyor.
- Exhaust gases from the cyclones are discharged to the primary scrubbers.



MAIN EQUIPMENT

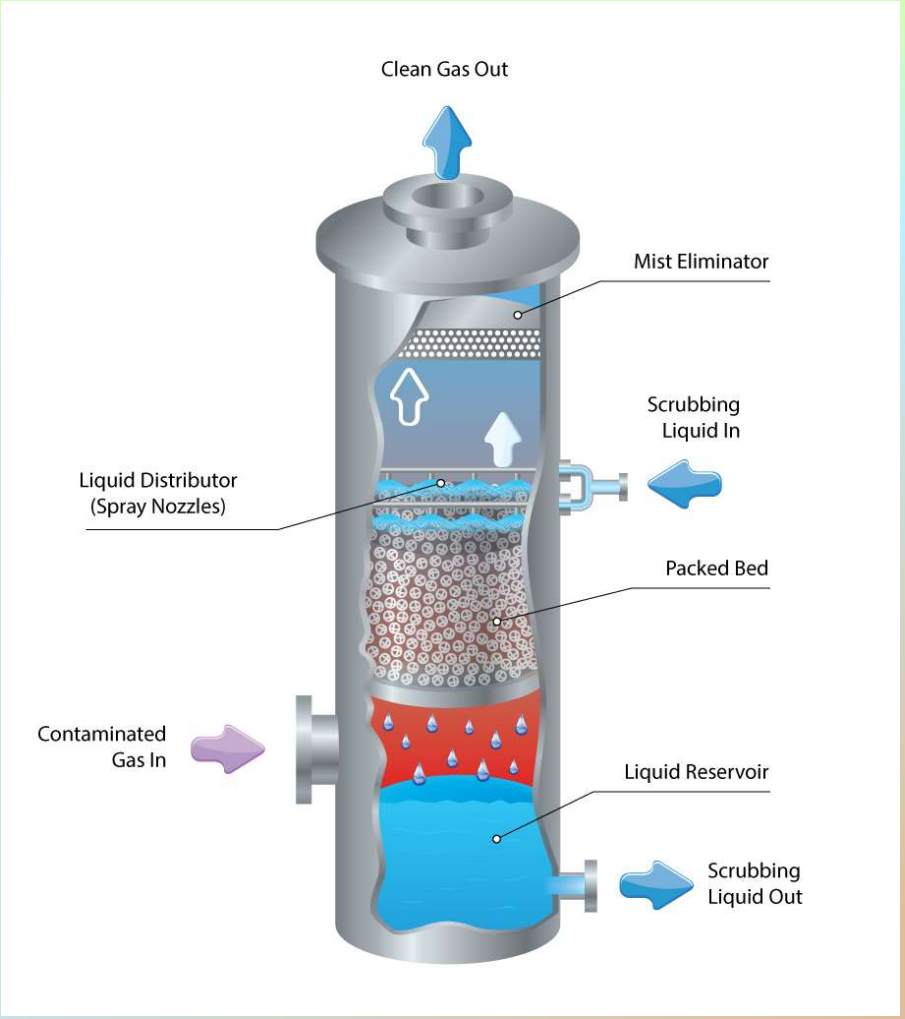
SCRUBBER

- Primary scrubbers

  1. One scrubber receives the vent gases from the reactor and granulator.
  2. One scrubber receives the vent air from the dryer.
  3. One scrubber receives other vent air as well as the vent air from the cooler.

- These scrubbers' function to remove any un- reacted ammonia and dust from the air streams.
- The air stream and low-pressure scrubber acid enter the venture portion of the scrubber.

SCRUBBER


Clean Gas Out
Mist Eliminator
Scrubbing
Liquid In
Liquid Distributor
(Spray Nozzles)
Packed Bed
Contaminated
Gas In
Liquid Reservoir
Scrubbing
Liquid Out

MAIN EQUIPMENT

- At the throat of the venture the exhaust stream has obtained a high velocity which generates an infinite mixing of gas and acid.
- The mixed stream then enter the cyclonic portion of scrubber where it is treated with a spray of high-pressure acid while being subjected to a centrifugal force which separates the acid from the gas.
- The-clean gas is then discharged to the tail-gas scrubber, while the scrubber acid is returned to the recycle tank.
- In the case of DAP production, the acid from the tank is phosphoric acid which reacts with NH_3 but in production of MAP water is used.

MAIN EQUIPMENT

- The exhaust from the primary scrubber system flows to the tail-gas scrubber where it receives further cleaning.
- The scrubbing medium is water.

MAIN EQUIPMENT

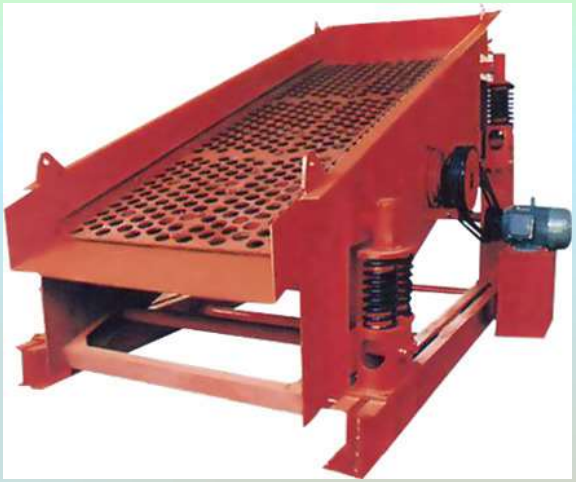
AMMONIA VAPORIZER

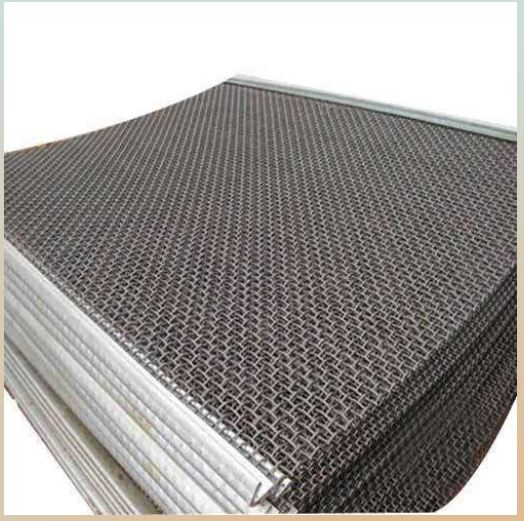
- The vaporizer converts liquid ammonia to vapor for use in the reactor.
- The exchanger is a horizontal shell and tube type with the steam on the tube side.

MAIN EQUIPMENT

SCREENS

1. Frame vibrating screen.
2. Mesh vibrating screen.





MAIN EQUIPMENT

AMMONIA TANK

- Ammonia is imported from several Arab and foreign countries by ships.
- It is pumped from ships through a 14 inch pipe to two storage tanks, the storage capacity of the first is (30,000) tons, and the second is (10,000) tons.
- Temperature inside the tanks is kept around (-33) ºC at one atmospheric pressure, using special compressors.

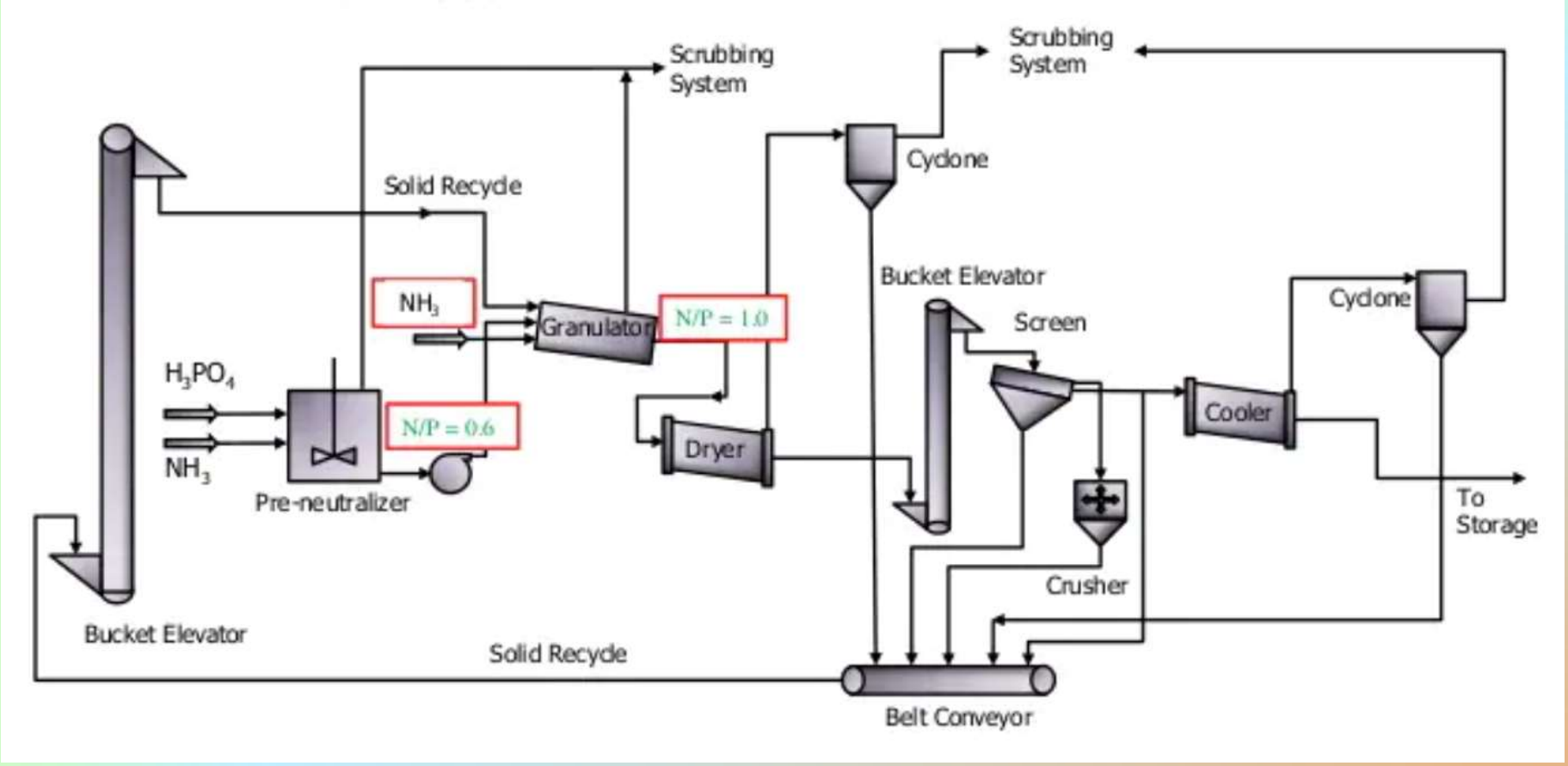
MAIN EQUIPMENT

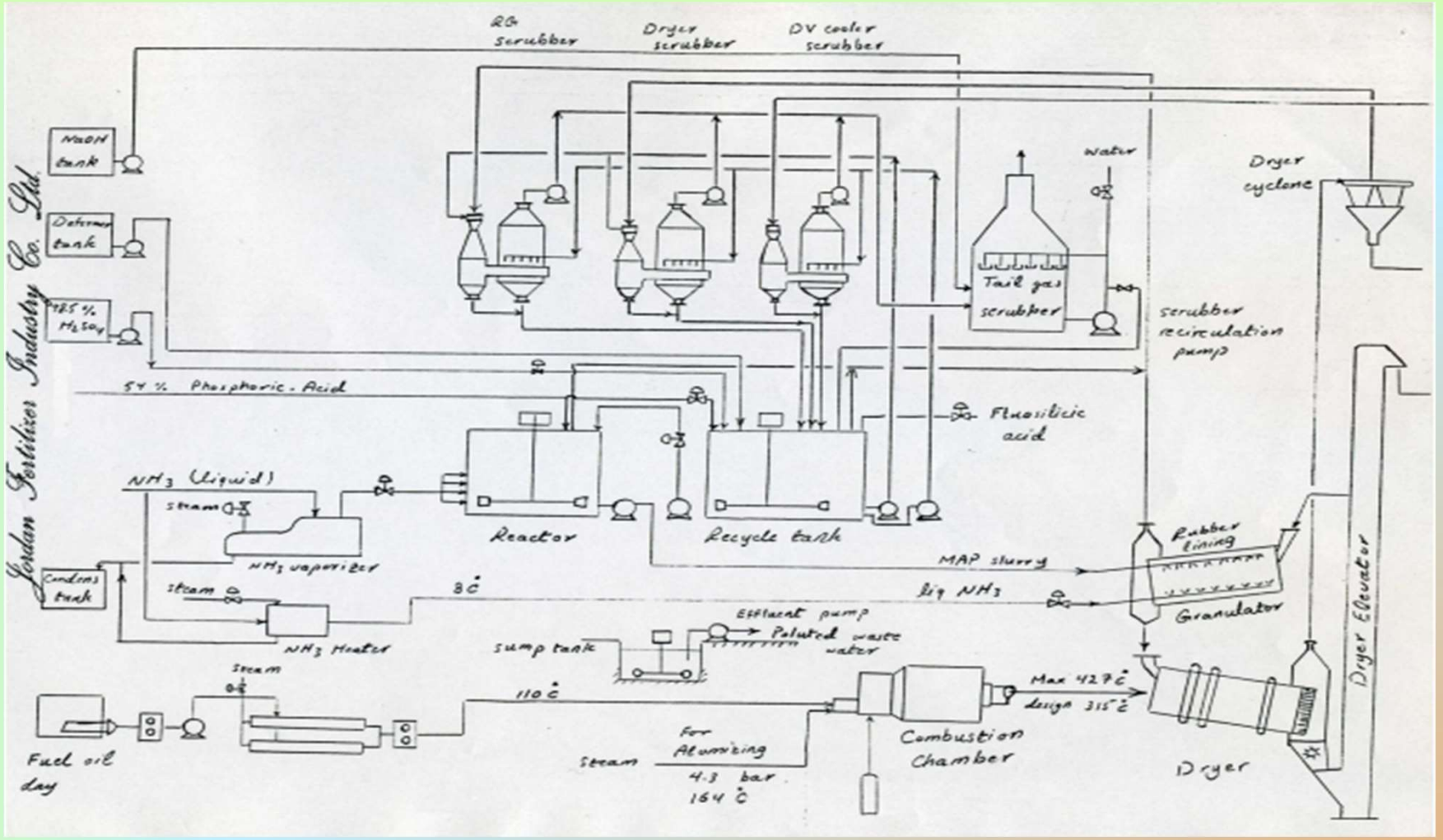
PROBLEMS:

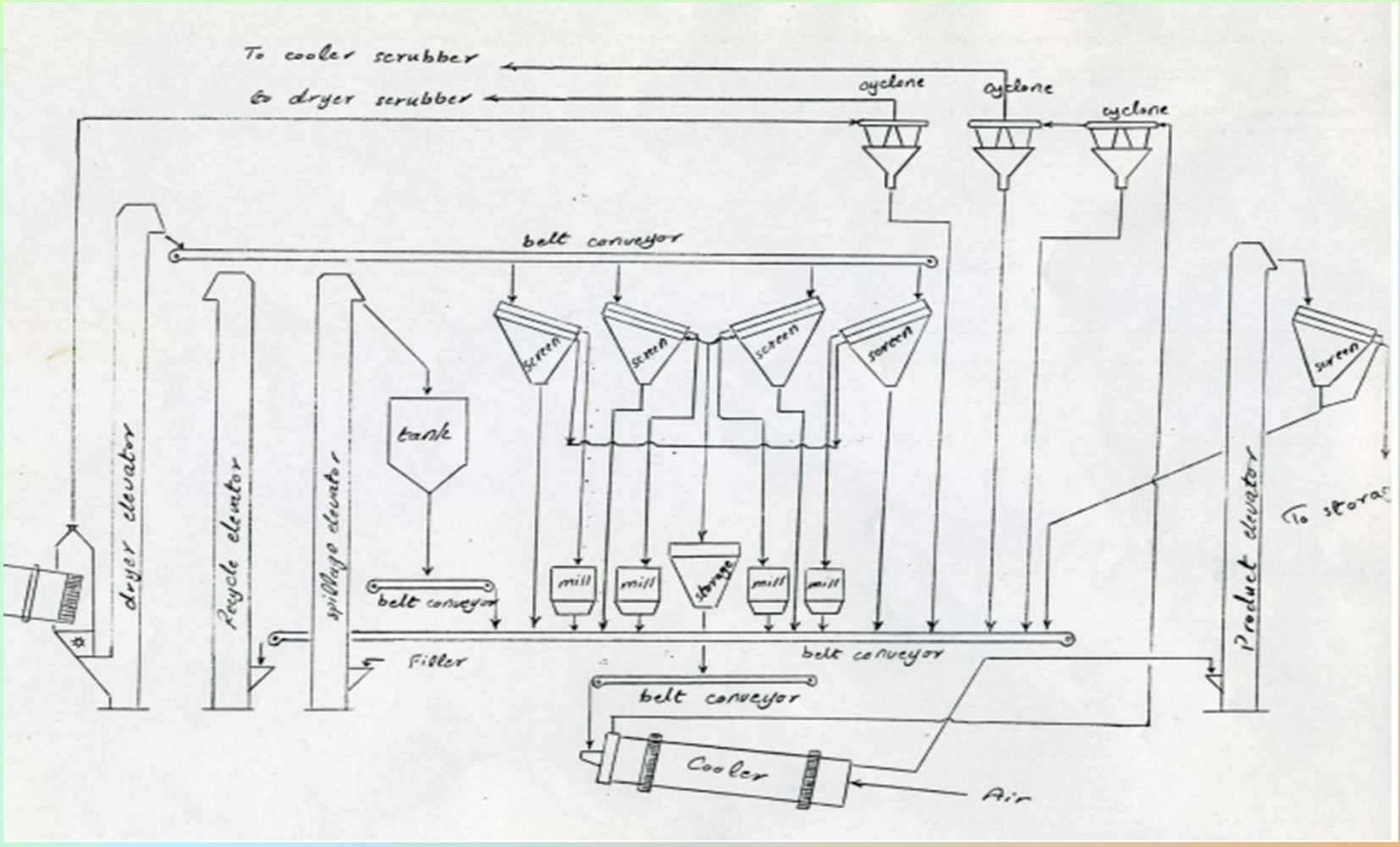
- To overcome any of the following problems:

1. High moisture: increase dryer heat.
2. Low N and low PH: increase ammonia flow (total).
3. Low P_2O_5: increase P_2O_5 (total).
4. All low analysis: decrease filler low.

DAP PRODUCTION FLOWSHEET




Jordan Fertilizer Industry Co. Ltd.
RG scrubber
Dryer scrubber
DV cooler scrubber
NaOH tank
Defoamer tank
98.5 % H_2SO_4
54 % Phosphoric Acid
Water
Dryer cyclone
Tail gas scrubber
Scrubber recirculation pump
Fluosilicic acid
NH_3 (Liquid)
Steam
NH_3 vaporizer
Reactor
Recycle tank
Rubber lining
MAP slurry
liq NH_3
Granulator
Condens tank
Steam
NH_3 Heater
80 C°
Effluent pump
Polluted waste water
Sump tank
Steam
110 C°
Max 427 C°
Design 315 C°
Dryer Elevator
Fuel oil day
Steam
For Atomizing
4.3 bar
164 C°
Combustion Chamber
Dryer


To cooler scrubber
To dryer scrubber
cyclone
cyclone
cyclone
belt conveyor
screen
screen
screen
screen
screen
tank
dryer elevator
Recycle elevator
spillage elevator
belt conveyor
mill
mill
storage
mill
mill
Fibler
belt conveyor
belt conveyor
Product elevator
To storage
Cooler
Air

TRIPLE SUPERPHOSPHATE

- One of the advantages of TSP is that it is the most highly concentrated straight solid phosphate fertilizer available, with 44% to 48% available P_2O_5 and 40% to 45% water-soluble P_2O_5.
- Another advantage is that part of its P_2O_5 content is derived directly from phosphate rock, a relatively low-cost source.
- The percentage of P_2O_5 in TSP that is derived directly from rock varies from about 25% to 30%, depending on the CaO : P_2O_5 ratio in the rock, the impurity of the rock and acid.

TSP DISADVANTAGES

- TSP has three main disadvantages:

1. The total nutrient content is lower than that of ammonium phosphate.
2. Its acidic character may cause deterioration of some types of bags.
3. It is not well suited for blending with urea because of reaction that cause deterioration of physical condition.

TSP PREPARATION

- TSP may be prepared in either granular or nongranular form.
- The non-granular form is preferred for use as intermediate for production of compound fertilizer by granulation process, whereas the granular form is preferred for direct application or for blending.
- The basic chemical reaction involved in production of TSP is as follows:

$$Ca_3(PO_4)_2 + 4H_3PO_4 + H_2O \longrightarrow 3Ca(H_2PO_4)_2.H_2O + 172.58\ kcal$$

- In most processes, a large percentage of the fluorine remains in the product, probably as fluosilicates and possibly as calcium fluoride.

TSP PREPARATION

- The proportion of acid to rock often is calculated to yield a P_2O_5 : CaO mole ratio of 0.95 to 1.0 (weight ratio – 2.41 to 2.54) according to the formula:

$$\frac{Acid\ P_2O_5 + Rock\ P_2O_5}{Rock\ CaO} = 2.41\ to\ 2.54\ (weight\ ratio)$$

- However, various impurities in the acid and rock cause variations in the optimum acid : rock ratio.

TSP BY DEN PROCESS

- The manufacture of TSP by this route involves the following operations:

1. Reaction:

✓ Very finely ground phosphate rock (95% to 98% < 100 mesh) is mixed with phosphoric acid.

✓ With rock of 34% P_2O_5 content, about 2.6 kg of acid is required per 1 kg of rock P_2O_5.

✓ The phosphoric acid used is merchant-grade acid at 52% P_2O_5 concentration.

TSP BY DEN PROCESS

2. Denning:

- ✓ The fluid material from the mixer goes to a Den where it solidifies.
- ✓ Solidification results from the continued reaction and crystallization of mono-calcium phosphate.
- ✓ The Denning times of 10-30 minutes are suitable for TSP.
- ✓ The Den must be enclosed and connected to a fume exhaust system to direct fluorine containing gases to a scrubber.

TSP BY DEN PROCESS

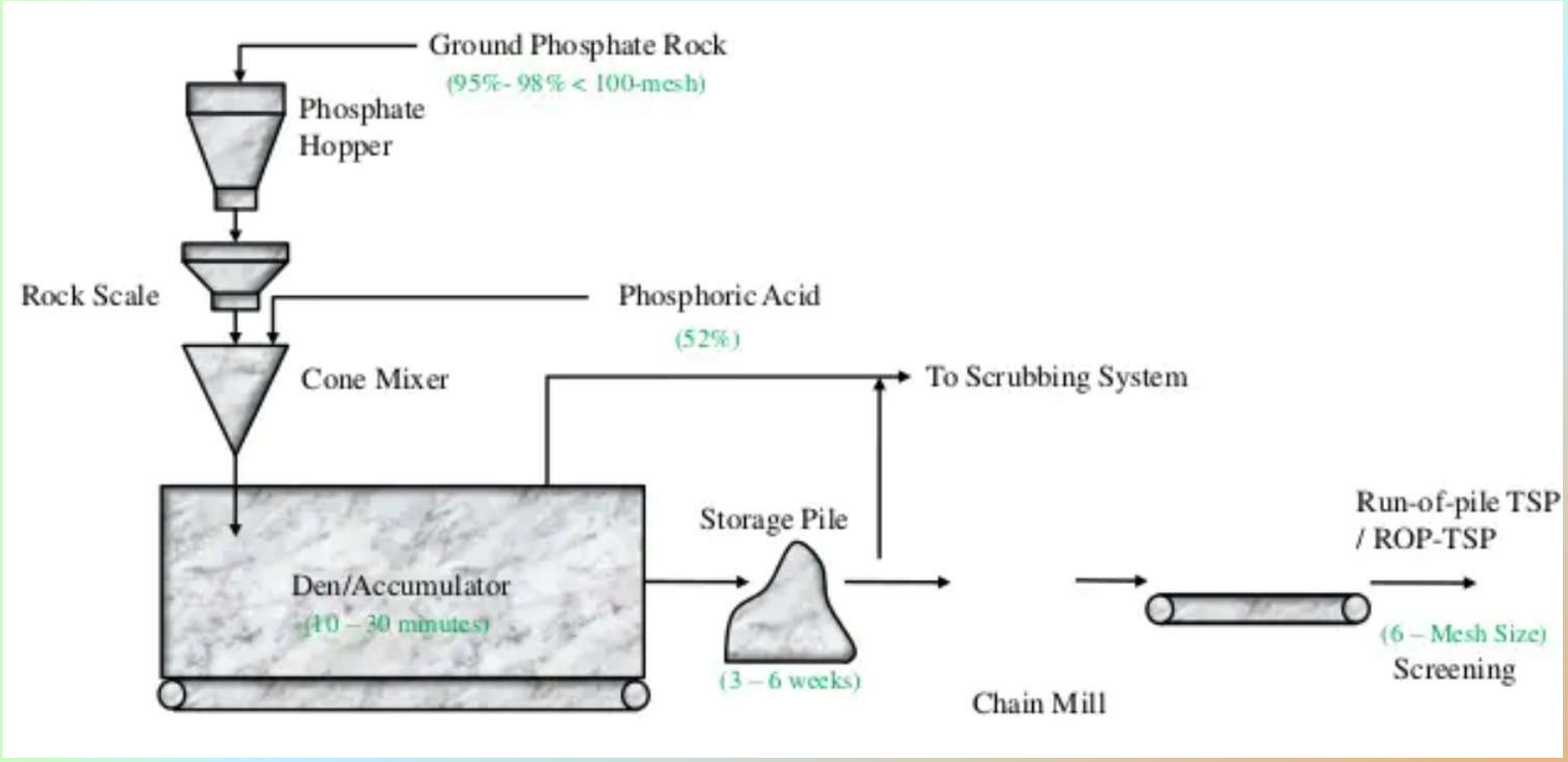
3. Storage/Curing:

- ✓ The product is removed from the Den and conveyed to storage piles for final curing which requires 3-6 weeks depending on the nature of the raw materials.
- ✓ During curing, the reaction approaches completion.
- ✓ The free acid, moisture and un-reacted rock contents decrease, and the available and water-soluble P_2O_5 content increase.
- ✓ Small amounts of fluorine compounds continue to be evolved during storage curing.

TSP BY DEN PROCESS

- A good ventilation is needed to remove the fluorine from the working area.
- Scrubbing exhaust gas may be necessary to prevent atmospheric pollution.
- After storage curing, the TSP is reclaimed with a power shovel and disintegrated in a cage or chain mill to pass 6-mesh screen (3.3 mm).
- The disintegrated TSP may be used for making compound fertilizer by agglomeration granulation, or it may be used as is for direct application.

TSP BY DEN PROCESS

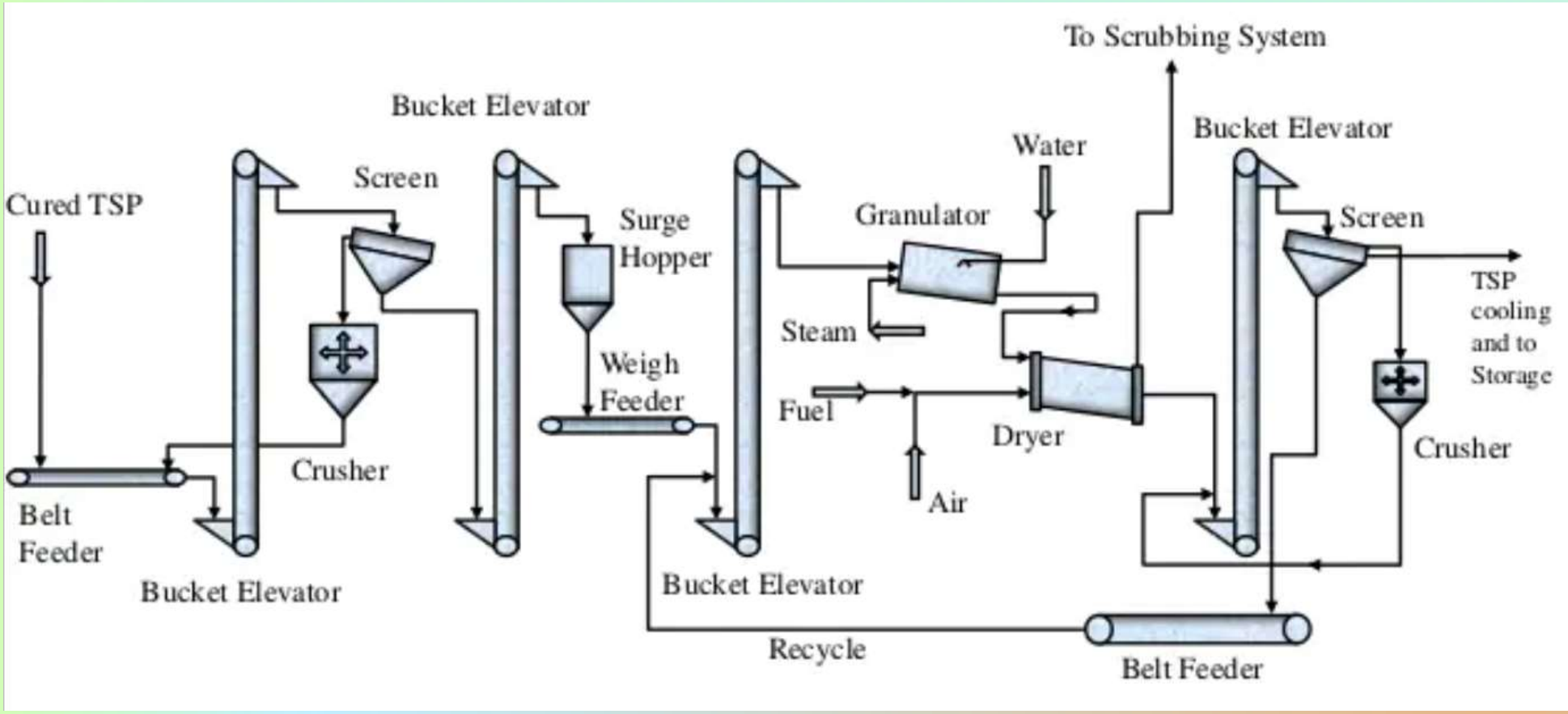


TSP BY DEN PROCESS

4. Granulation:

- Granulation of powder or cured TSP is granulated by the process shown on figure.
- After milling and screening, the cured powder TSP is conveyed to a rotary drum granulator.
- Water is sprayed onto the bed of material and steam is sparged underneath the bed to provide wet granular material.
- The wet granules are discharged to a rotary dryer.
- The dried granules are screened, and the oversize is milled and returned with the fines to the granulator.

GRANULATION OF CURED TSP



TSP BY DEN PROCESS

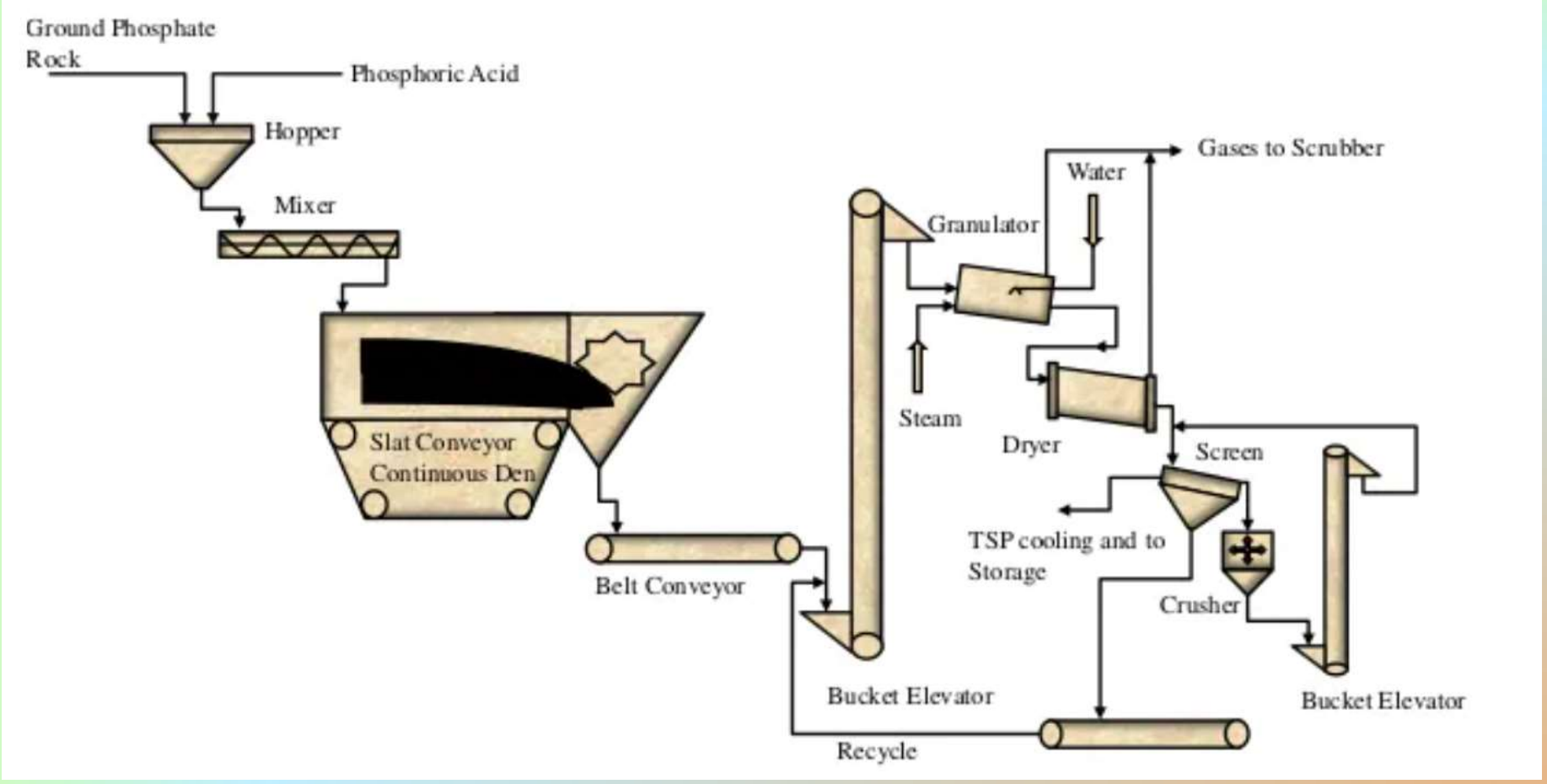
- Dust and fumes from the dryer are scrubbed in a water scrubber.
- Alternatively, dust may be removed by a big filter prior to the wet scrubbing.

Inputs	Construction per tone product
Cured TSP, Ton	1.02
Steam, kg	75
Cooling water, kg	250
Fuel, GJ	0.67
Electric energy, kWh	29
Operating labor, work hours	0.3

EX-DEN GRANULATION

- The acidulation and Denning steps are similar to those described for producing non-granular TSP except that the rock may be somewhat more finely ground, and the Den retention time is longer (25 – 45 minutes vs 10 – 30 minutes).
- Also, the product from the Den goes directly to a granulator rather than to storage.
- After granulation, the product is dried, screened, and conveyed to storage.
- Drying is controlled to yield a product of 4% - 6% moisture.

EX-DEN GRANULATION OF TSP

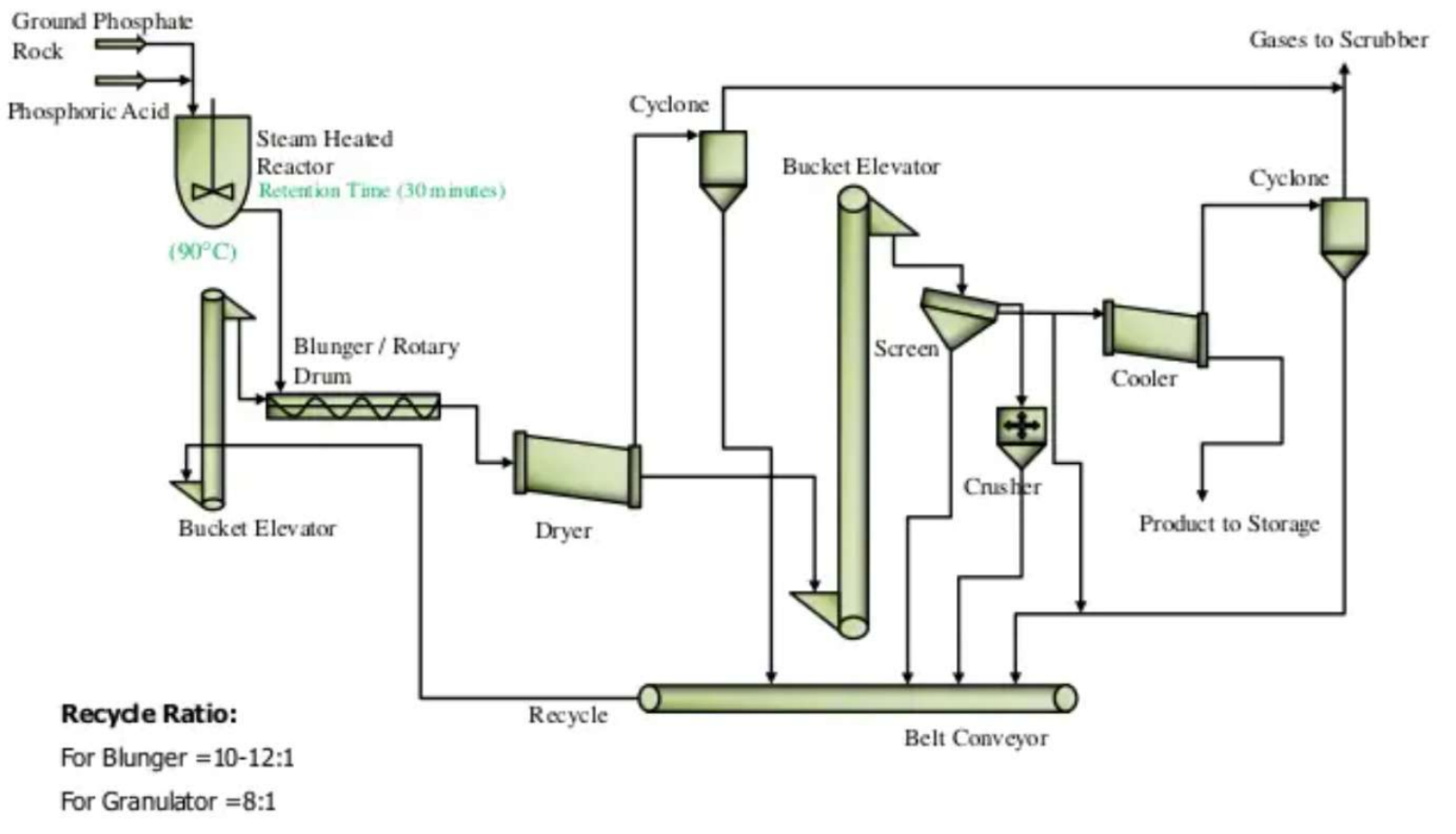


DIRECT SLURRY GRANULATION

- When granules TSP is the desired end product, it is usually preferable to produce it directly rather than by granulation of powder TSP.
- Some advantages of direct granulation processes are:

1. Cost is usually lower.
2. Granules are denser and stronger.
3. Granulation equipment can be used interchangeably for producing TSP and ammonium phosphates.

DIRECT SLURRY GRANULATION



DIRECT SLURRY GRANULATION

There are two main disadvantages of direct granulation:

1. Owing to the limited reaction time, un-reactive rocks are poorly suited for use in the direct granulation process.
2. Greater losses of soluble P_2O_5 may occur owing to incomplete reaction, or a higher ratio of phosphoric acid to phosphate rock may be needed to prevent this loss.

NON-GRANULAR MAP

- In most cases, the product is made in large plants located adjacent to phosphoric acid plants.
- Often the product is shipped to smaller granulation plants for use as raw materials to be granulated with others in an agglomeration granulation of compound fertilizers.
- Many processes for making non-granular MAP have been developed.
- In general, all processes aim at a simple, low-cost method by eliminating granulation, recycling, and drying.

NON-GRANULAR MAP

- However, the product should have sufficiently good physical properties to permit storage, handling, and transportation without excessive caking or dust problems.
- MAP powder is the most concentrated P_2O_5 (52%) product and can be considered as an important component for the production of complex fertilizers.

Powder

Crystalline

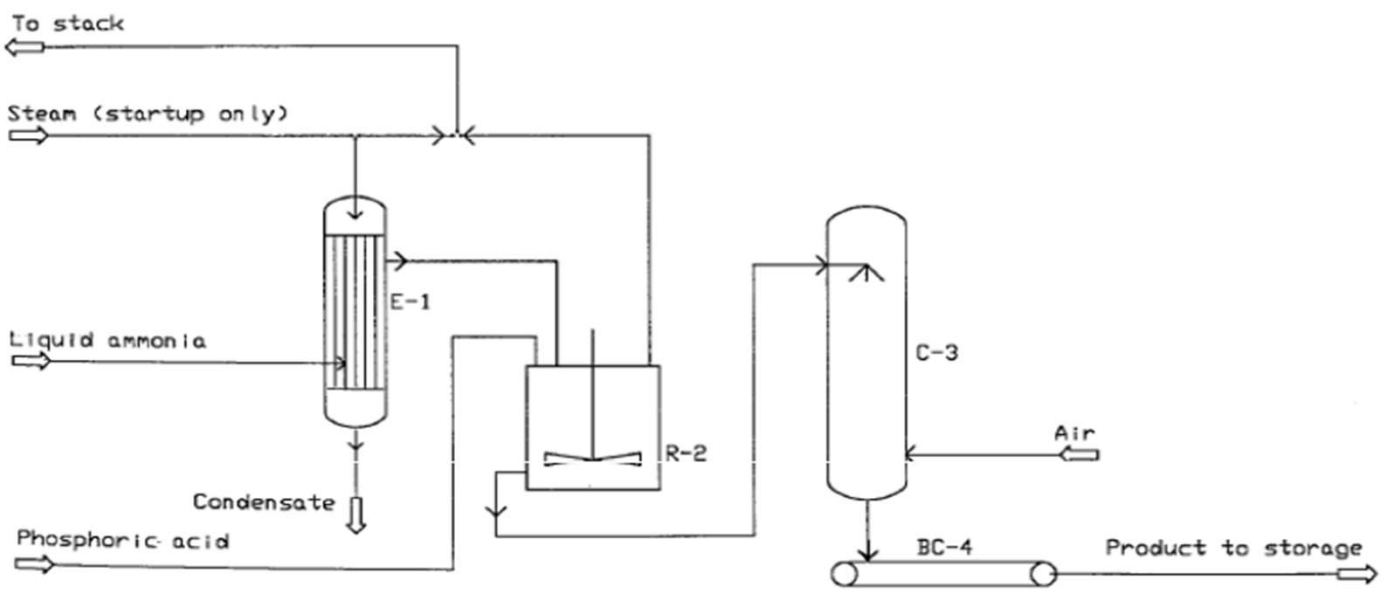
FISONS PROCESS

- In the Fisons process, phosphoric acid of about 50% P_2O_5 concentration is reacted with gaseous ammonia under 2.1 kg/cm^2 gauge pressure.
- The heat of reaction drives off part of the water as superheated steam.
- The remaining slurry contains 9% - 10% water, the temperature is 170^{o}C, and the pH is 3.5 – 4.0.
- This hot slurry is released into a spray tower through a special spray nozzle.

FISONS PROCESS

- More water is flashed off and evaporates as the droplets cool and solidify by falling through an ascending airstream.
- The product contains about 6% moisture; the grade range from 10-50-0 to 12-56-0, depending on the impurity content of the acid.
- The product is in the form of small round particles ranging from 0.1 to 1.5 mm.

FISONS PROCESS

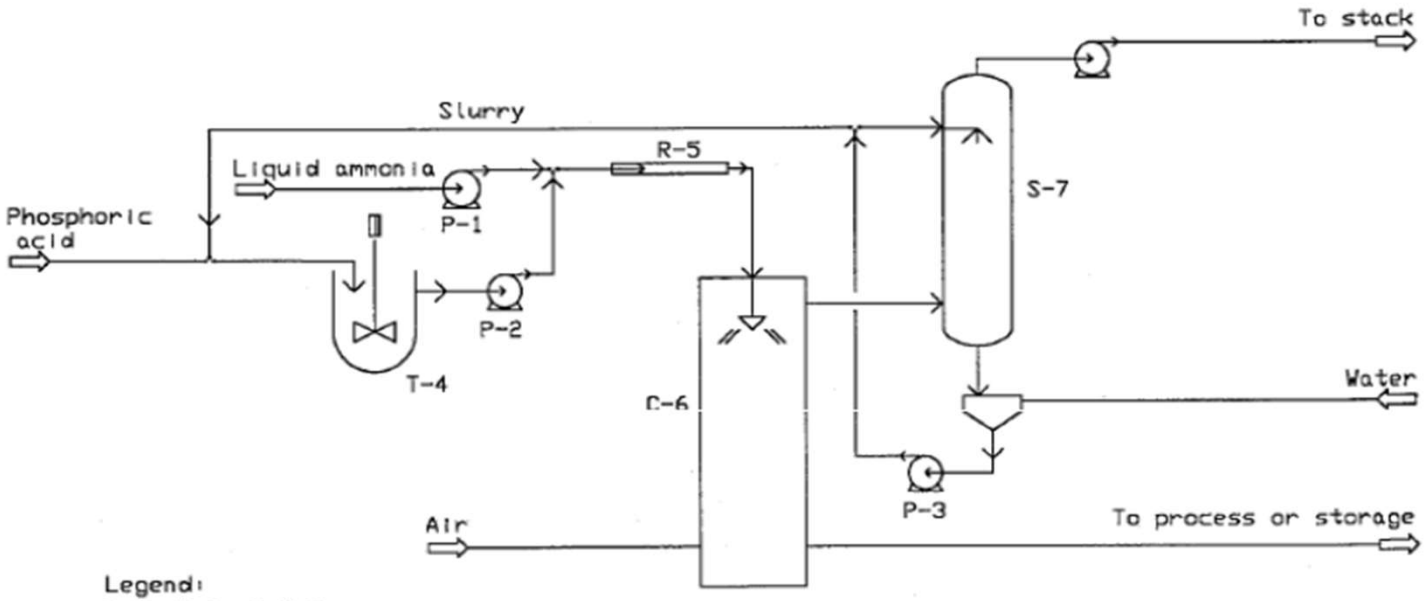


Fisons "Minifos" Process.

SWIFT PROCESS

- In the Swift process, phosphoric acid (50% P_2O_5) and liquid ammonia react in a two-fluid nozzle, which discharges into a reactor pipe.
- The mixture of finely divided MAP and steam is injected into a cooling tower where a countercurrent airstream carries away the water vapor formed by the heat of reaction and cools the product.
- The product moisture content is 3% - 5%.

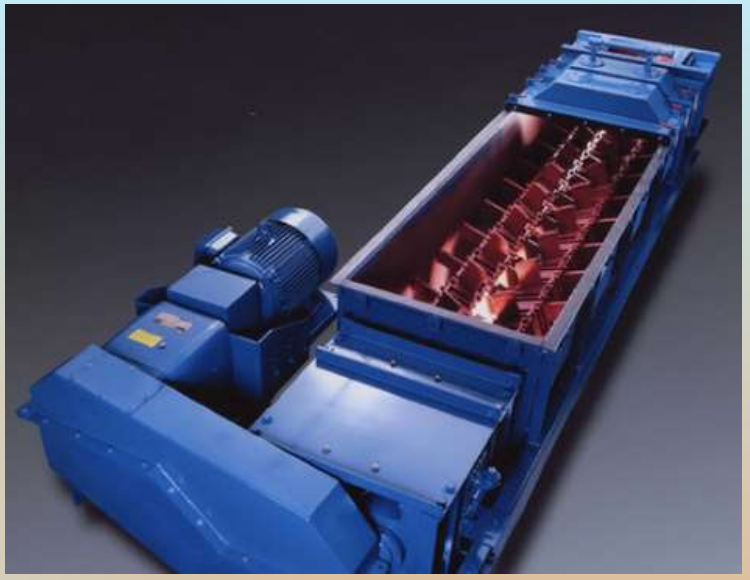
SWIFT PROCESS



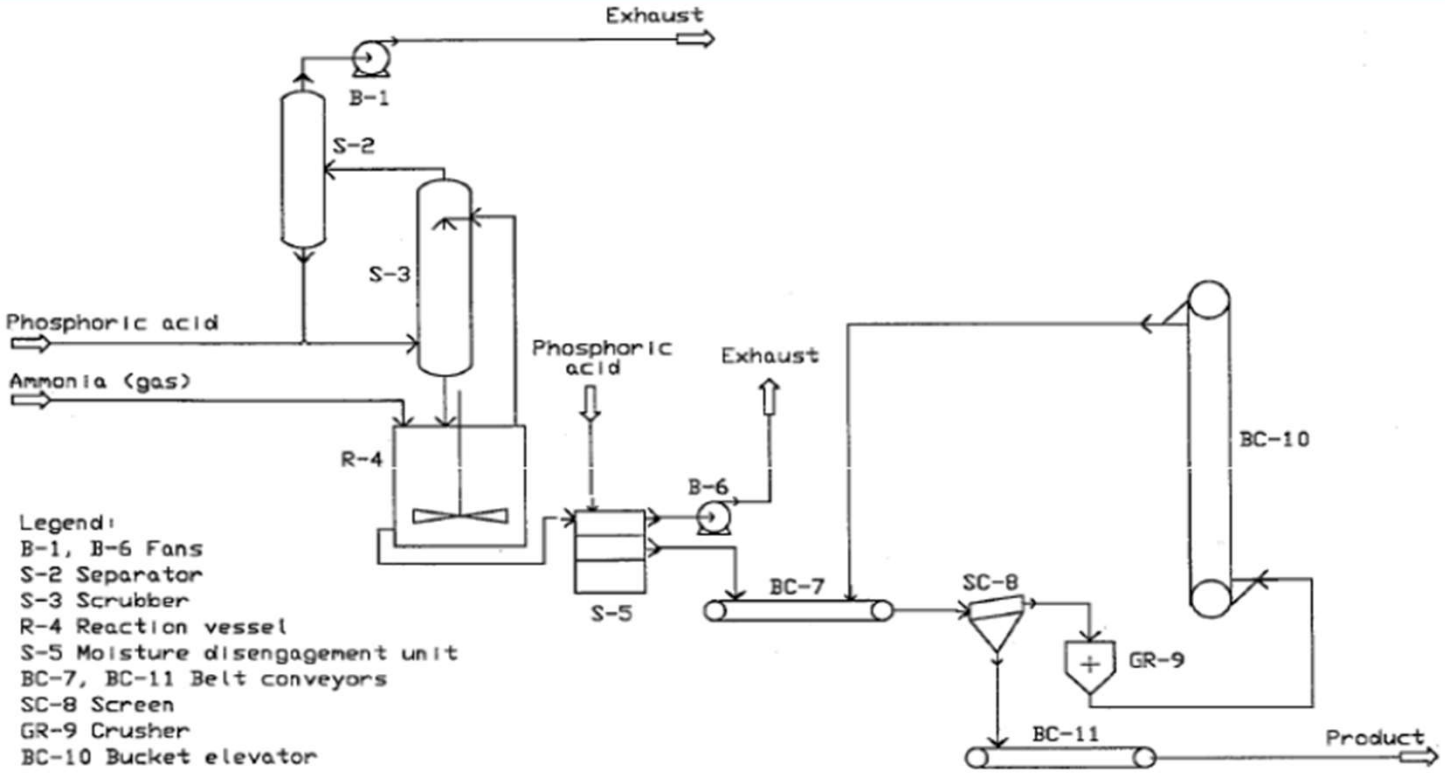
Swift Powder MAP Process.

SCOTTISH AGRICULTURAL INDUSTRIES PROCESS

- This process consists of a reaction vessel in which phosphoric acid (about 50% P_2O_5) is neutralized with ammonia to a mole ratio of about 1.35, and the resulting hot slurry is mixed with more phosphoric acid in a specially designed twin-shafted mixer somewhat like a pugmill, which disintegrate the mass into small particles releasing water vapor.
- The product typically contains 6% moisture, 11% N, and 50% water-soluble P_2O_5.



SCOTTISH AGRICULTURAL INDUSTRIES PROCESS



SAI Process for Producing Nongranular MAP.